

Intensification of oxidation capacity using chloroalkanes as additives in hydrodynamic and acoustic cavitation reactors

Anand G. Chakinala^a, Parag R. Gogate^b, Rashmi Chand^a, David H. Bremner^{a,*}, Raúl Molina^c
and Arthur E. Burgess^a

^aSchool of Contemporary Sciences, University of Abertay Dundee, DD1 1HG Dundee,
United Kingdom

^bInstitute of Chemical Technology, University of Mumbai, Matunga, Mumbai, 400019 India

^bDepartment of Chemical and Environmental Technology, School of Experimental Sciences
and Technology, Rey Juan Carlos University, 28933 Mostoles, Madrid, Spain

* Corresponding author: Tel.: +44 1382 308667; Fax: +44 1382 308663

E-mail: d.bremner@abertay.ac.uk (David H Bremner)

Abstract

The effect of the presence and absence of the chloroalkanes, dichloromethane (CH_2Cl_2), chloroform (CHCl_3) and carbon tetrachloride (CCl_4) on the extent of oxidation of aqueous I^- to I_3^- has been investigated in (a) a liquid whistle reactor (LWR) generating hydrodynamic cavitation and (b) an ultrasonic probe, which produces acoustic cavitation. The aim has been to examine the intensification achieved in the extent of oxidation due to the generation of additional free radicals/oxidants in the reactor as a result of the presence of chloroalkanes. It has been observed that the extent of increase in the oxidation reaction is strongly dependent on the applied pressure in the case of the LWR. Also, higher volumes of the chloroalkanes favour the intensification and the order of effectiveness is $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$. However, the results with the ultrasonic probe suggest that an optimum concentration of CH_2Cl_2 or CHCl_3 exists beyond which there is little increase in the extent of observed intensification. For CCl_4 , however, no such optimum concentration was observed and the extent of increase in the rates of oxidation reaction rose with the amount of CCl_4 added. Stage wise addition of the chloroalkanes was found to give marginally better results in the case of the ultrasonic probe as compared to bulk addition at the start of the run. Although CCl_4 is the most effective, its toxicity and carcinogenicity may mean that CH_2Cl_2 and CHCl_3 offer a safer viable alternative and the present work should be useful in establishing the amount of chloroalkanes required for obtaining a suitable degree of intensification.

Keywords: Ultrasound, LWR, Potassium iodide oxidation, Dichloromethane, Chloroform, Carbon tetrachloride, Intensification

1. Introduction

As a result of the greater public awareness about the impacts of the detrimental effects of organic pollutants and the more recent stringent environmental legislation, the last decade has seen a rise in the number of reports on the degradation of organic pollutants in wastewaters using different advanced oxidation technologies [1]. Cavitation is one such process that has been studied for the degradation of organic compounds in wastewater [2] wherein, highly reactive free radical formation takes place as a result of generation of micro bubbles and their subsequent collapse due to pressure field variations in the solution. The collapse of the cavitation bubbles leads to formation of hotspots (local areas of high temperature and pressures) resulting in homolytic cleavage of molecules and the formation of free radicals such as HO^\bullet , H^\bullet , HO_2^\bullet and, also, H_2O_2 and other oxidizing species in the liquid phase depending on the constituents of the liquid e.g. presence of chloroalkanes. Cavitation can be induced in a solution by passage of ultrasound (acoustic cavitation) or by subjecting the liquid to velocity variations by introducing constrictions in the flow (hydrodynamic cavitation). However, cavitation reactors, in particular ultrasonic reactors, often give lower efficiency of degradation at larger scales of operation and it is usually necessary to intensify the oxidation reaction in order to treat industrial wastewater on the large-scale. Several studies have been reported for the enhancement of oxidation capacity in the reactor in terms of concentration of free radicals and/or oxidants and consequently the rates of oxidation reactions. Use of high frequencies [3], multiple frequency transducers [4], purging gases into the reaction vessel [5,6], addition of heterogeneous catalysts [7] and aqueous additives such as salt [8] have all been investigated in order to facilitate reactions induced by cavitation, where the controlling mechanism is free radical attack. It has been observed that investigations have been mostly limited to sonochemical reactors and no literature reports can be found where the effect of additives to intensify the rate of oxidation reactions in the case of hydrodynamic cavitation reactors has been investigated.

Due to the limitations of the use of ultrasound, particularly for continuous reactions on an industrial scale, hydrodynamic cavitation (HC) has been investigated as an alternative for the degradation of organic pollutants in wastewater. In this process, liquid jets at high velocities are forced to pass through small constrictions

thereby forming micro bubbles, the implosion of which, downstream of the constriction, results in hydroxyl radical formation. Suslick et al. described [9] the chemistry induced by high-pressure hydrodynamic cavitation whereas Kalumuck et al. [10] have reported the use of HC for wastewater treatment. Pandit and co-workers have also reported several studies using HC and, in particular, have described the use of multiple orifice plates [11-13].

Chloroalkanes can be a useful additive in improving the efficacy of both acoustic cavitation and hydrodynamic cavitation especially when the controlling mechanism is free radical attack. The first report on the effect of ultrasound on haloalkanes dates back to 1950 when Weissler described the ultrasonic reaction of CCl_4 in aqueous solution [14] and later work [15, 16] showed that simple haloalkanes were also susceptible to the effects of ultrasound enhancing the overall oxidation capacity in the reactor. Investigations on sonoluminescence intensity also confirmed that CCl_4 undergoes decomposition to HCl and HOCl in the presence of ultrasound [17]. There are reports indicating the use of CCl_4 for enhancing the degradation rates of different pollutants such as phenol, methyl orange [18-20] and also in the degradation of aqueous solutions containing KI and NaCN [21]. However, the use of lower chloroalkanes for intensification of oxidation reactions has not been reported and, to our knowledge, no research exists describing the use of any chloroalkanes in the case of hydrodynamic cavitation reactors. It should be also noted here that concentration of chloroalkanes should be optimized in such a way that the entire amount of additives is used in the degradation process and there should not be any residual additives in the effluent stream. Literature reports [22-25] clearly indicate that ultrasonic irradiation results in degradation of CCl_4 and other lower chloroalkanes, hence the concentration of chloroalkanes to be used in the reactor should be such that the sonochemical degradation of added chloroalkanes is complete. Laboratory scale optimization is recommended to establish this optimum concentration unless data is available in the reported literature for similar operating conditions.

Considering the toxicity and carcinogenicity of CCl_4 [26] the current study demonstrates the use of less toxic chloroalkanes and its comparison with CCl_4 in hydrodynamic (LWR) and acoustic cavitation (ultrasonic probe) reactors. The

effectiveness of different chloroalkanes, in terms of degree of intensification achieved has been quantified by means of the I^-/I_3^- dosimeter.

2. Experimental

2.1. The Liquid Whistle Reactor (LWR)

A LWR is an inline, homogenizing device which is coupled to a positive displacement pump and is employed in a comprehensive system containing the motor, variable frequency drive, pressure and flow measuring devices [27]. The LWR consists of a feed vessel tank with a 5 L capacity, a plunger pump (Giant Industries, Model P220A, USA) with a power consumption of 3.6 kW and having a speed of 1750 rpm and a mixing chamber comprising of an orifice (orifice area, $7.74 \times 10^{-7} \text{ m}^2$) and a blade (length, 0.0268 m; width, 0.0222 m; thickness, 0.0015 m). The pump has a maximum discharge pressure of up to 2000 psi. The distance between the orifice and blade is adjustable and the backpressure valve connected at the end of the mixing chamber influences the pressure.

The presence of the orifice generates a high velocity liquid jet, which is projected over the edge of blade, kept adjacent to the orifice. The process liquid sheds vortices perpendicular to the original flow in between the orifice and blade, creating a steady oscillation, which imposes pressure fluctuations on the cavitating bubbles. The use of a blade also creates a situation similar to the use of two orifices in the system, which results in an increase in the extent of cavitation. In a typical run in the LWR, 4 L of KI solution (20g/L) in deionised water was prepared and pumped through the orifice at selected pressures for given times, with and without, added chloroalkanes. Aliquots (2 mL) were withdrawn every 10 min during the reaction for analysis using a UV-VIS spectrophotometer (Jenway 6300) and then returned to the reaction vessel after measurement. The amount of I_3^- production was determined using the molar absorptivity at 355 nm. The temperature was maintained constant at $35 \pm 3 \text{ }^\circ\text{C}$ using an external cooling ice bath. Lower temperatures, even though desired, could not be achieved even after using ice cooling.

2.2. Ultrasonic probe

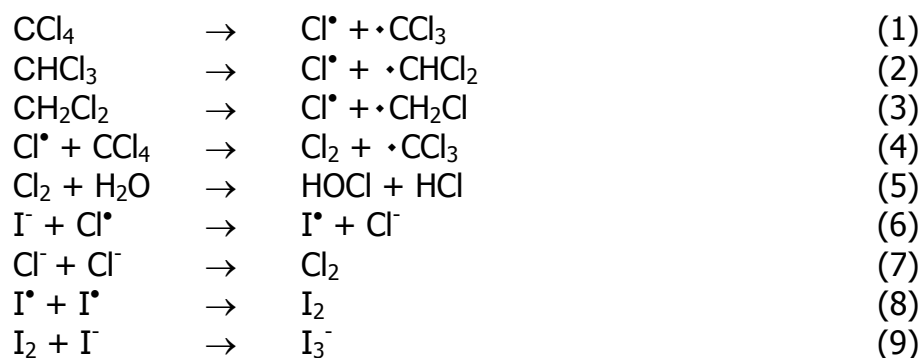
Experiments were carried out using a commercial ultrasonic processor (Cole Parmer) equipped with a titanium probe (1 cm diameter) capable of operating either continuously or in a pulse mode at a fixed frequency of 20 kHz with amplitude set to

25% (supplied power input=90 W; the actual power dissipation into the solution estimated using calorimetric measurements was about 36 W). In the present work, experiments were carried out with 200 mL of the working solution in a 300 mL glass beaker and subjected to sonication in a pulse mode with 4.0 sec of power on and 2.0 sec of power off in order to allow the system to dissipate some of the heat generated by the ultrasonic waves in the reaction vessel. The ultrasonic probe was immersed into the reaction vessel containing aqueous KI solution (20g/L concentration) at a constant depth (0.025 m into the solution). The temperature was maintained constant at 23 ± 2 °C throughout the reaction using an external cooling ice bath. For experiments with the haloalkanes: CH_2Cl_2 , CHCl_3 and CCl_4 , different concentrations of additives were added to the KI solution and mixed well prior to sonication. The range of concentrations of the additives was selected such that heterogeneity was introduced in the system. Heterogeneous conditions provide additional nuclei and increase the number of cavitation bubbles generated in the system leading to expected intensification. An earlier study by Rajan et al. [28] indicated that for 0.5 cm^3 of CCl_4 in a total of 10 cm^3 of mixture (9.5 cm^3 KI solution), the number of cavitation bubbles was equal to 3.432×10^{10} while the value was 2.04×10^{10} in the absence of CCl_4 . In the current study, all experiments were carried out in triplicate to check the reproducibility and the average values are shown. Experimental errors were in the range of $\pm 5\%$.

3. Results and Discussion

It is known that during cavitation, microbubbles are formed which collapse violently producing high temperatures and pressures leading to the production of free radical species such as $\cdot\text{OH}$, $\text{H}\cdot$, $\text{O}\cdot$ and, also, H_2O_2 . This process is enhanced by the presence of haloalkanes [14-21, 28-29], which degrade in presence of cavitating conditions to release $\text{Cl}\cdot$ radicals that also take part in the desired reactions and intensify the rates. In addition to the $\text{Cl}\cdot$ radicals actually taking part in the oxidation process, they also undergo a series of recombination reactions resulting in the formation of additional oxidizing agents, such as Cl_2 and HOCl [28] and these contribute to the expected overall intensification of the oxidation rates. The molecules Cl_2 and HOCl formed in the system are much more stable than the free

radicals and hence are expected to contribute more though it is not possible to exactly quantify the role played by each oxidant. The possible mechanisms occurring in the cavitating bubble, bubble/water interface and/or bulk water can be outlined below:



It is conceivable that the Cl^\bullet generated from the decomposition of the chloroalkanes [7,25-26], at the organic/water interface, takes part in the overall oxidation process through a number of radical chain reactions (reactions depicted by equations 1-5 above are just the initiation reactions for formation of the additional oxidizing species due to the presence of chloroalkanes). For a detailed account of the radical reactions taking place in the presence of CCl_4 and KI, the work of Rajan et al. [28] is recommended.

Expected oxidation reactions due to the presence of hydroxyl radicals formed during the cavitation events also occur simultaneously in the system. Earlier work of Gogate et al. [30] and Prasad Naidu et al. [31] has clearly demonstrated that KI is oxidized due to the generation of hydroxyl radicals in the system in both sonochemical as well as hydrodynamic cavitation reactors. The presence of chloroalkanes gives additional free radicals for oxidation reactions in the form of Cl^\bullet and also further oxidizing agents (Cl_2 and HOCl formed as a result of recombination reactions) resulting in overall intensification in the extent of oxidation.

3.1 The Liquid Whistle Reactor (LWR)

Initial studies conducted in the LWR, with no added chloroalkanes, showed that no oxidation of I^- to I_3^- was apparent even at 1500psi operating pressure. This is probably due to the fact that the intensity of cavitation produced in the reactor is not capable of generating enough hydroxyl radicals required for the oxidation of KI

coupled with the fact that lower flow rates lead to fewer passes through the cavitating zone. Also, any hydroxyl radicals generated in the system might not diffuse into the liquid phase for favourable reaction with the KI leading to expected oxidation. The rates of diffusion and mixing are expected to be substantially lower in the present system due to low circulation flow rates. Suslick et al. [9] have reported a similar requirement of a minimum intensity of cavitation for the onset of oxidation in that no liberation of iodine was observed below 150 bar pressure even in a CCl_4 saturated environment. However, it should be noted here that use of multiple orifice plates has been reported to give substantial rates of oxidation of KI even at very low pressures in the range of 1-7 bar [11,12,30]. The use of multiple orifice plates leads to the generation of a greater number of cavitation bubbles due to the presence of additional instabilities. Also the range of liquid circulation flow rates (attributed to design of the orifice chamber in terms of free area available for flow and use of a bypass line) used in earlier work [11,12,30] is substantially higher as compared to the present work resulting in enhanced diffusion and mixing rates. It can be concluded that the design of hydrodynamic cavitation reactors is a crucial factor in deciding the range of operating parameters for a particular application. Efficient design of the reactor allows generation of enough free radicals/oxidizing species so as to initiate the desired application even at substantially lower operating pressures, which eventually reduces energy consumption and operational costs.

In the presence of CH_2Cl_2 , oxidation to I_3^- was observed even at lowest operating pressure of 500psi, though the effect was marginal compared to higher operating pressures (Figure 1). Thus the role of CH_2Cl_2 in intensifying the overall extent of oxidation capacity (generation of additional oxidant species by recombination reactions) has been confirmed. It can be seen that the amount of I_3^- production increased linearly with time and with increasing pressures ranging from 500 to 1500 psi. The observed increase in the rates of oxidation at higher inlet pressures can be attributed to higher intensity of cavitation at higher inlet pressures as observed using the bubble dynamics studies [32]. Higher intensity cavitation leads to enhanced degradation of the chloroalkanes generating higher quantum of the oxidizing species (Cl^\bullet , Cl_2 and HOCl). The net effect of these enhanced concentrations of oxidizing species is increased rates of oxidation at higher inlet pressures. At 500 psi, the rate of I_3^- production was very low when compared with higher pressures at 100 min of reaction time and continuing the circulation through

the orifice for a further 100 min at 500 psi showed no further change in I_3^- production. When the solution is subjected to the higher pressure of 1000 psi, the oxidation rate was faster and increased gradually with time though a pressure of 1200 psi showed a further marginal positive effect. However at 1500 psi the rate was 8 times that of the 500 psi and it is interesting to note that the rate of oxidation is substantially higher over the first 10 min. Higher rates of oxidation at initial time can be attributed to presence of the dissolved gases initially, which are subsequently degassed due to the cavitation. Once the system is degassed, the oxidation proceeds at a steady rate, which is controlled by the rate of free radical production. Kumar et al. [12] have reported similar results for the oxidation of KI in a hydrodynamic cavitation setup with multiple orifice plates.

The effect of the same amount (5.25 g/L concentration) of different volatile chlorinated additives on oxidation using the LWR at 1500 psi is shown in Figure 2 in terms of the rate constant for I_3^- liberation. It can be seen that the oxidation rate is maximum in the presence of CCl_4 and decreases from $CHCl_3$ to CH_2Cl_2 . The rates of oxidation with CCl_4 are approximately 2 and 6 times higher when compared with $CHCl_3$ and CH_2Cl_2 respectively using the LWR and probably reflect the Cl^\bullet availability under the conditions used. Thus even if CCl_4 is toxic and carcinogenic, it is most effective in intensifying the sonochemical reactions. Use of a particular intensifying parameter for cavitation applications can be decided on by considering the local environmental regulations and also on whether any residual chloroalkanes remain after the end of the treatment.

In order to verify whether the same degree of intensification, as compared to CCl_4 , could be achieved using higher volumes of dichloromethane, experiments were performed using a higher concentration of CH_2Cl_2 (7 g/L) with other conditions remaining the same and the results, shown in Figure 3, are compared with the earlier dataset (concentration of 5.25g/L). The rates of oxidation did not increase much as compared with the lower concentration of CH_2Cl_2 though the time required to reach saturation in the I_3^- production increased marginally. To explain the idea of saturation time in terms of I_3^- production, or in other words, time required for exhaustion of the Cl^\bullet availability, results with varying volumes in the case of $CHCl_3$ (higher availability of Cl^\bullet as compared to CH_2Cl_2) are also shown in Figure 3. Two different concentrations of $CHCl_3$ (1.75 g/L and 5.25g/L) were used to study the effect of the

amounts of CHCl_3 on the oxidation of I^- at 1500 psi. Interestingly, when the reaction was carried out with the lower amount of CHCl_3 , the reaction rate stopped increasing after 30 min, probably due to the low concentration of CHCl_3 remaining at this time. At the higher amount of CHCl_3 the extent of oxidation continuously increased since chlorine atoms (and other radicals/oxidizing species) were still being produced within the experimental timescale. The results also confirm that the additives are being degraded in the reactor and the concentration can be adjusted so that no residual chloroalkanes are present in the final discharge stream.

3.2 *The Ultrasonic probe*

Three different sets of experiments were carried out with the ultrasonic probe using different amounts of dichloromethane (1.4 to 7g/L) and the results were compared with the conditions of no dichloromethane. There was very little increase in the amount of I_3^- produced with time of operation when only aqueous iodide was subjected to sonication as compared to the presence of chloroalkanes for all three cases of CH_2Cl_2 addition. The initial rate of I_3^- production with ultrasound alone was found to be (0.10 $\mu\text{mol}/\text{min}$), which is approximately 10 times less than that observed with the addition of dichloromethane at the lowest concentration. Higher loading of CH_2Cl_2 did not result in any increase in the rate of I_3^- production; on the contrary it decreased at higher loadings as evident from figure 4. The observed optimum concentration of CH_2Cl_2 is very similar to that seen for other additives, such as hydrogen peroxide, resulting in an increase in the overall oxidation capacity [33].

The observed decrease can be explained on the basis of alteration of the liquid physico-chemical properties as well as the effect of additives on the intensity of cavitation. It is expected that the concentration of CH_2Cl_2 will be elevated compared to that of H_2O in the cavitating bubble at higher concentrations of CH_2Cl_2 . Earlier energy analysis studies have indicated that presence of higher vapour content in the system leads to a decrease in the energy released during the cavitation phenomena [34]. The decrease in the energy released has been attributed to presence of vapours in the cavity which lowers the overall adiabatic gas constant of the gases present inside the cavity. Also, Rae et al. [35] have reported that the temperature pulse generated due to the collapse of the cavity (measure of the cavitation intensity) decreases with an increasing concentration of the aqueous solutions.

Similar results of quenching of sonoluminescence in the presence of aqueous solutions have been reported by Ashokkumar et al. [36] and Barbour et al. [37]. It should be noted that the use of additives would also alter the liquid phase physico-chemical properties and, in turn, affect the intensity of cavitation occurring in the system. In particular, alterations of surface tension affect bubble cloud behavior changing key processes such as collapse and coalescence; causing significant decreases in the overall efficiency of the process. Thus, the intensity of cavitation generated in the system will be lower at very high concentrations of CH_2Cl_2 leading to a decrease in the effective extent of dissociation of CH_2Cl_2 thereby decreasing the concentration of the oxidizing species.

Thus, in the case of sonication also, higher concentrations of dichloromethane as a replacement to CCl_4 are not recommended. In the case of hydrodynamic cavitation, a decrease in the rate of I_3^- production was not observed possibly due to the low intensity of cavitation as compared to acoustic cavitation.

Stepwise addition of dichloromethane (thus maintaining lower concentrations of dichloromethane at any given time) were also investigated. The average rate of I_3^- production, when the entire amount of dichloromethane was added initially, was $0.88 \mu\text{M}/\text{min}$. Stepwise addition of dichloromethane resulted in an increase in this average rate of I_3^- production to $1.1 \mu\text{M}/\text{min}$. This phenomenon can be attributed to the fact that the source for chlorine radicals, which controls the overall oxidation process, is continuously renewed and would avoid complete depletion of the chlorine radicals in the system, which is normally observed when all the chloroalkane is added at the start of the reaction.

The addition of chloroform also had a significant effect on the oxidation of KI at low concentrations and the rate constant did not increase with a further change in the concentration of CHCl_3 from 1.4 to 7g/L. The rate constants of I_3^- production were $2.83 \mu\text{M}/\text{min}$, $2.95 \mu\text{M}/\text{min}$, and $2.79 \mu\text{M}/\text{min}$ when the amounts of CHCl_3 were varied over the range specified (figure 5). As compared to dichloromethane, the rate constant for I_3^- production did not decrease significantly at higher volumes of CHCl_3 due to higher availability of Cl^\bullet per mole of degradation of CHCl_3 . In this case, though the intensity of cavitation decreases thereby lowering the extent of dissociation of CHCl_3 , enhanced production of Cl^\bullet per mole of CHCl_3 degradation

somewhat balances the decreased dissociation thereby resulting in a marginal decrease in the overall production of I_3^- .

Support for the hypothesis of the greater availability of Cl^\bullet , as discussed earlier, can be obtained by the results obtained with CCl_4 . An increase in the concentration of CCl_4 over same range gives a continuous increase in the rate of oxidation as shown in Figure 5. This can be attributed to the fact that the amount of Cl^\bullet radicals formed by the degradation of the CCl_4 is substantially higher as compared to the scavenging action caused by a decrease in the intensity of cavitation at higher concentration of the additives. Exact quantification of Cl^\bullet radical formation was not possible but the trends observed with dichloromethane, chloroform and CCl_4 (varying amounts over the same range as shown in figure 5) definitely support this hypothesis. Also, based on the oxidation-reduction thermodynamics, CCl_4 is considered to be non-reactive with hydroxyl radicals and reactions would proceed through reductive processes rather than chemical oxidations [38]. Thus, the rate of I_3^- formation in the presence of CCl_4 is directly proportional to the rate of Cl^\bullet radical formation, which is again directly proportional to the degradation of CCl_4 .

A comparison of the efficacy of chloroalkanes is represented in figure 5, which shows the relative rates of oxidation of I^- by the sonic probe in the presence of equal amounts of the chloroalkanes. It can be seen that in the absence of any chloroalkanes the rate of oxidation is quite low and the rate increases considerably in the order dichloromethane to chloroform to carbon tetrachloride. Quantitatively, the rate of I_3^- production is 45 times, 28 times and 10 times more for the addition of CCl_4 , $CHCl_3$, and CH_2Cl_2 as compared to that when no chloroalkanes were added. The results obtained are identical to that obtained with the hydrodynamic cavitation indicating that the mode of generation of cavitation does not play any role in deciding the efficacy of the chloroalkanes.

Effectiveness of cavitation also appears to depend on the amount of the chloroalkane present relative to the amount of bulk aqueous iodide solution. The chloroalkanes do not dissolve in the solution but exist as micro droplets dispersed throughout the bulk aqueous phase and this dispersion multiplies the number of nucleating sites available for cavitation. An exact quantification of the number of cavities in the presence and absence of CCl_4 reported by Rajan et al. [28] clearly

confirms the enhanced number of cavitation events occurring in the system. Any increase in the concentration of chloroalkanes results in a decrease in the intensity of cavitation as discussed earlier. Thus, use of chloroalkanes for intensifying the oxidation capacity is recommended only up to an optimum concentration, which can be established by laboratory scale studies according to the guidelines presented in the present work.

3.3 Comparison of Hydrodynamic Cavitation and Acoustic Cavitation:

Initially, acoustic cavitation generated using an ultrasonic probe appears to be around 5 times more effective in terms rate of oxidation of I^- to I_3^- as compared to the hydrodynamic cavitation reactor under, otherwise, similar conditions. This is not the true picture, however, as the extent of the energy dissipated and volume of the reactants is an order of magnitude different in each case. A true comparison should be made in terms of the oxidation rate constant per unit power density where the latter is defined as the electrical energy dissipated into the system per unit volume of the reactant. However, calculation of the oxidation rate constant per unit power density still indicates that the acoustic cavitation is about 2.5 times more effective as compared to the hydrodynamic cavitation. The result is contradictory to some of the reported results in the literature [39-41] and can be attributed to the difference in the design of the hydrodynamic cavitation unit, operating conditions in terms of use of by-pass for the cavitation chamber, the relatively high operating pressures and the low circulation flow rates in the case of the hydrodynamic cavitation reactor used in the present work.

4. Conclusions

The oxidation of I^- using a LWR and an ultrasonic probe in the presence and absence of different chlorinated compounds such as CH_2Cl_2 , $CHCl_3$ and CCl_4 has been studied. The LWR with no additives under the given set of operating conditions did not facilitate progress of the oxidation reaction, possibly attributed to inefficient design and operation of the hydrodynamic cavitation setup. Comparison with the literature gives supporting information though the exact value of the onset pressure for beneficial effects is strongly dependent on the design of hydrodynamic cavitation

reactor. The results obtained with the LWR, in the presence of dichloromethane, indicated that the degree of intensification is directly proportional to the applied pressure and maximum rates of I_3^- production were obtained with a LWR at 1500 psi. Studies with different chloroalkanes indicated the order of effectiveness in terms of intensification of oxidation reaction as $CCl_4 > CHCl_3 > CH_2Cl_2$. However, using higher concentrations of $CHCl_3$ or CH_2Cl_2 did not give better results as compared to CCl_4 .

In the case of the ultrasonic probe a similar trend in terms of effectiveness of chloroalkanes was observed. Also there appears to be a decrease in the reaction rates with an increase in the amount of CH_2Cl_2 added but no similar change in the rates of reaction was observed when the concentration of $CHCl_3$ was similarly varied. The relative rates of oxidation were higher in the presence of CCl_4 when compared to $CHCl_3$ and CH_2Cl_2 . Stepwise addition of CH_2Cl_2 resulted in marginally better results as compared to addition of the total amount at the start of the experiment.

Comparison of acoustic and hydrodynamic cavitation reactors indicated that under the operating and geometric conditions used in the present work, the former was 2.5 times more efficient in the oxidation of I^- to I_3^- considering the relative energy consumption and scale of operation.

Overall, it can be said that chloroalkanes as additives enhance the oxidation capacity of cavitational reactors by generation of additional oxidizing species in the liquid phase due to recombination reactions of free radicals generated in the cavitation phenomena. Such additional oxidizing species in the liquid phase is highly beneficial for oxidation of non-volatile pollutant species which are less susceptible to free radical attack due to lower stability of the generated free radicals. The concentration of the additives must be optimized so that there is no residual chloroalkanes present in the final discharge effluent stream.

Acknowledgements

We wish to acknowledge the support from the University of Abertay Dundee (UAD) for this work. Also Proof of Concept (AGC) and European Social Fund (RC) are greatly acknowledged for the funding of this project. PRG wishes to acknowledge the support of Department of Science & Technology, India and The Royal Society, UK for sponsoring the visit to University of Abertay Dundee under the India UK Science Networks Scheme.

5. References

1. S. Parsons Ed., Advanced oxidation processes for water and wastewater treatment, IWA Publishing, London, UK, 2004.
2. T. Mason and C. Petrier, Chapter 8. in S. Parsons Ed., Advanced oxidation processes for water and wastewater treatment, IWA Publishing, London, UK, 2004.
3. M.H. Entezari and P. Kruus, Ultrason. Sonochem. 1 (1994) S75–S79.
4. A.V. Prabhu, P.R. Gogate, A.B. Pandit, Chem Eng. Sci, 59 (2004) 4991.
5. C. Petrier, A. Jeunet, J.L. Luche, and G. Reverdy, J. Am. Chem. Soc, 114 (1992) 3148
6. A. Kumar, P.R. Gogate, A.B. Pandit, A.M. Wilhelm, H. Delmas, Ultrason. Sonochem. 12 (2005) 453
7. A.B. Pandit, P.R. Gogate, S. Mujumdar, Ultrason. Sonochem. 8 (2001) 227.
8. J.D. Seymour, R.B. Gupta, Ind. Eng. Chem. Res. 36 (1997) 3453.
9. K.S. Suslick, M.M. Mdleleni, J.T. Ries, J. Am. Chem. Soc. 119 (1997) 9303.
10. K.M. Kalumuck, C-T. Hsiao, G.L. Chahine, J-K. Choi, Fifth International symposium on Cavitation, Osaka Japan, November 1-4 (2003) 1.
11. N.P. Vichare, P.R. Gogate, A.B. Pandit, Chem. Eng. Technol. 23 (2000) 683.
12. P.S. Kumar, M. Sivakumar, A.B. Pandit, Chem. Eng. Sci. 55 (2000) 1633.
13. M. Sivakumar, A.B. Pandit, Ultrason. Sonochem. 9 (2002), 123
14. A. Weissler, H.W. Cooper, S. Snyder, J. Am. Chem. Soc. 72 (1950) 1769.
15. A.V.M. Parke, D. Taylor, J. Chem. Soc. (1956) 4442.
16. B.H. Jennings, S.N. Townsend, J. Phys. Chem. 65 (1961) 1574.
17. P.K. Chendke and H.S., Fogler, J. Phys. Chem. 87 (1983) 1362.
18. N.N. Mahamuni, A.B. Pandit, Ultrason. Sonochem. 13 (2006) 165
19. W. Zheng, M. Maurin, M. A. Tarr, Ultrason. Sonochem. 12 (2005) 313.
20. L. Wang, L. Zhu, W. Luo, Y. Wu, H. Tang, Ultrason. Sonochem. 14 (2007) 253
21. I.Z. Shirganonkar, A. B. Pandit, Ultrason. Sonochem. 4 (1997) 245.
22. C. Petrier, A. Francony, Ultrason. Sonochem. 4 (1997) 295.
23. A. Francony, C. Petrier, Ultrason. Sonochem. 3 (1996) S77.
24. A Bhatnagar, M. Cheung, Env. Sci. Technol. 28 (1994) 1481
25. H.M. Cheung, A. Bhatnagar, G. Janson, Env. Sci. Technol. 25 (1991) 1510
26. <http://www.inchem.org/documents/ehc/ehc/ehc208.htm>

27. <http://www.sonicmixing.com/>
28. R. Rajan, R. Kumar, K.S. Gandhi, Chem. Eng. Sci. 53 (1998) 255
29. I. Hua, M.R. Hoffmann, Env. Sci. Technol. 30 (1996) 864
30. P.R. Gogate, I.Z. Shirgaonkar, M. Sivakumar, P. Senthilkumar, N.P. Vichare, A.B. Pandit, AIChEJ. 47 (2001) 2326
31. D.V. Prasad Naidu, R. Rajan, R. Kumar, K.S. Gandhi, V.H. Arakeri, S. Chandrasekaran, Chem. Eng. Sci. 49 (1994) 877
32. P.R. Gogate, A.B. Pandit, AIChEJ. 46 (2000) 1641
33. P.R. Gogate, A.B. Pandit, Adv. Env. Res. 8 (2004) 553
34. N.P. Vichare, P. Senthilkumar, V.S. Moholkar, P.R. Gogate, A.B. Pandit, Ind. Eng. Chem. Res. 39 (2000) 1480
35. J. Rae, M. Ashokkumar, O. Eulaerts, C. von Sonntag, J. Reisse, F. Grieser, Ultrason. Sonochem. 12 (2005) 325–329
36. M. Ashokkumar, R. Hall, P. Mulvaney, F. Grieser, J. Phys. Chem. B 101 (1997) 10845
37. K. Barbour, R.A. Caruso, F. Grieser, J. Phys. Chem. B 103 (1999) 9231.
38. A.L. Teel, R.J. Watts, J. Haz. Mat. B 94 (2002) 179
39. M. Sivakumar, A.B. Pandit, Ultrason. Sonochem. 9 (2002) 123
40. K.M. Kalumuck, G.L. Chahine, J. Fluids Eng. 122 (2000) 465
41. S.S. Save, A.B. Pandit, J.B. Joshi, Chem. Eng. J. 55 (1994) B67

List of Figures:

Fig. 1: Effect of pressure on the oxidation of I^- in the presence of CH_2Cl_2 using a LWR. (Experimental conditions: Volume - 4L; KI - 20g/L; CH_2Cl_2 - 5.25g/L; Temperature - $35 \pm 5^\circ C$)

Fig. 2: The effect of different chlorinated additives (5.25g/L of each) on the rate of I_3^- production using LWR. (Experimental conditions: pressure - 1500 psi; volume of solution - 4L; KI - 20g/L; temperature - $35 \pm 5^\circ C$).

Fig. 3: Comparison of different amounts of CH_2Cl_2 and $CHCl_3$ on the rate of I_3^- production using LWR.

Fig. 4: Comparison of the effect of different amounts of chloroalkanes on the rate of I_3^- production using the ultrasonic probe.

Fig. 5: Amount of I_3^- production using the ultrasonic probe in the presence of different chloroalkanes.

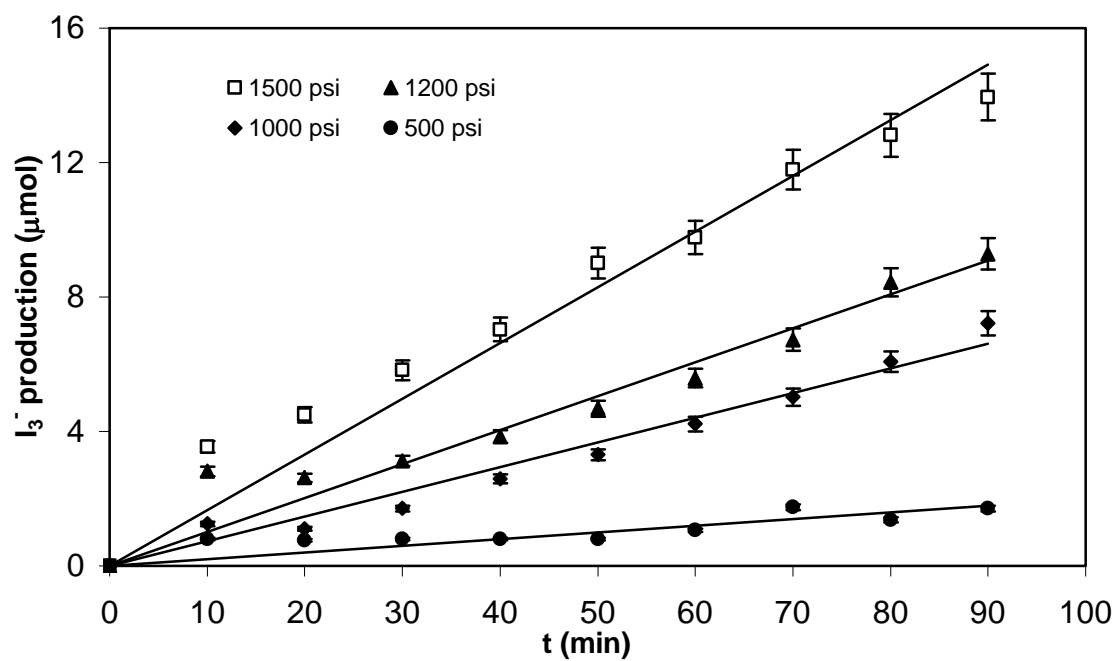


Fig. 1:

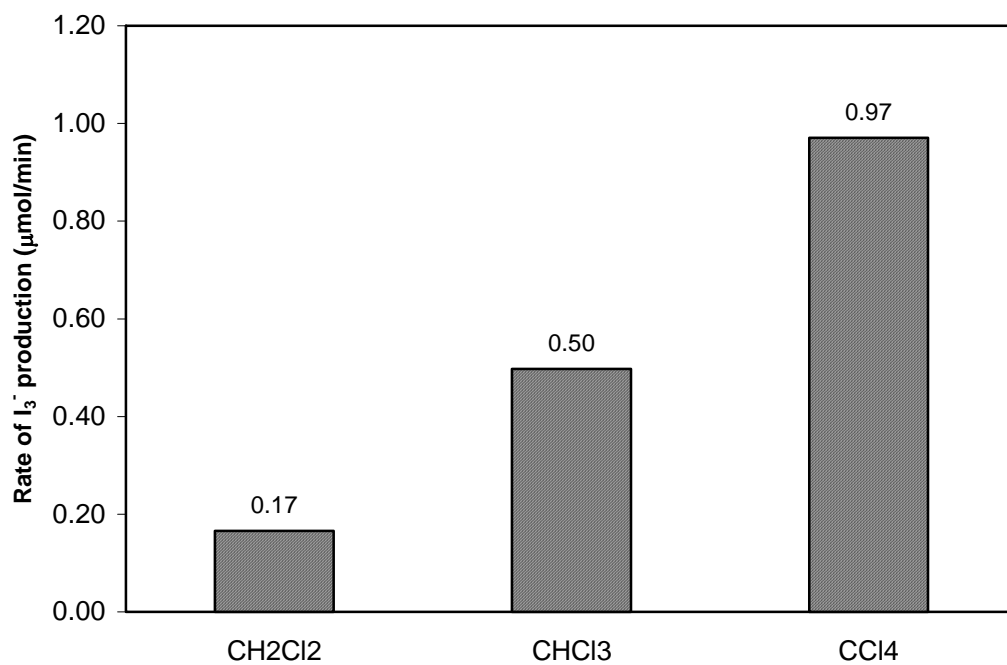


Fig. 2:

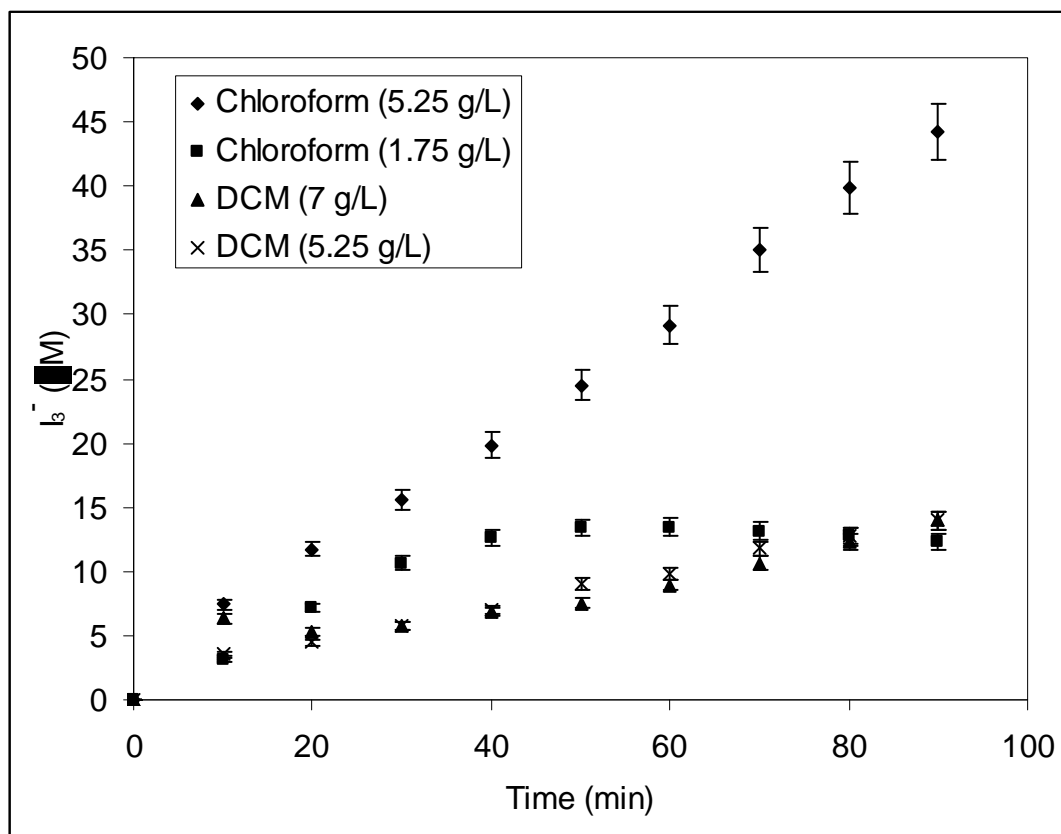


Fig. 3:

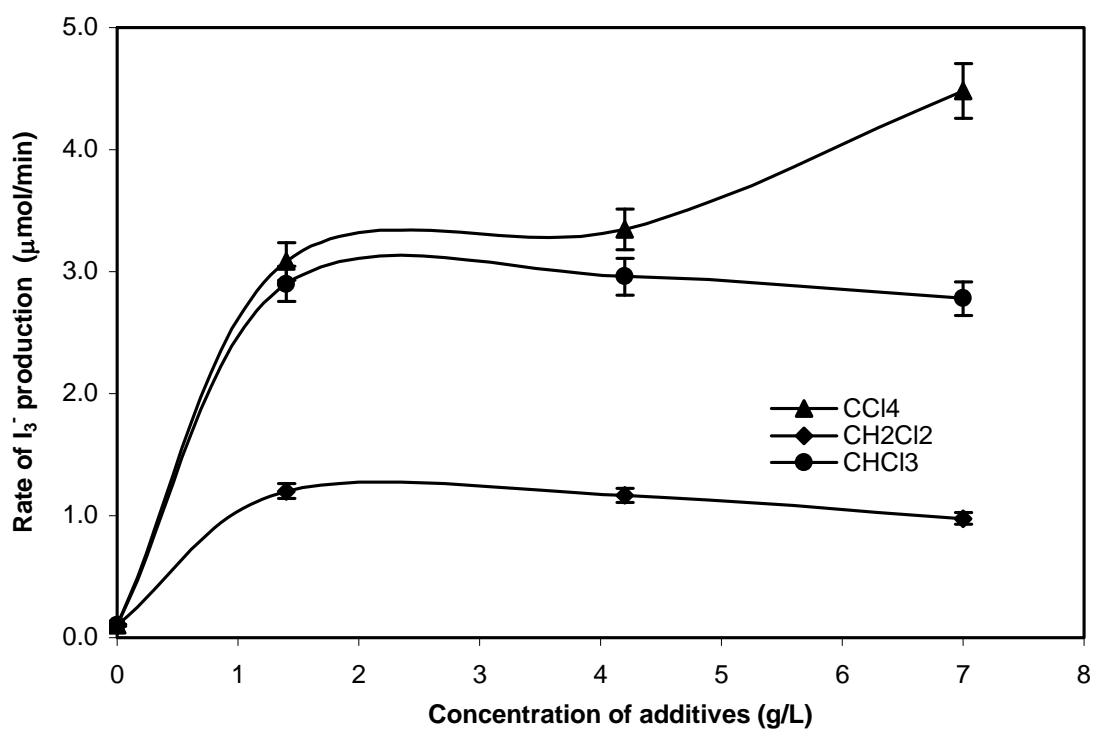


Fig. 4:

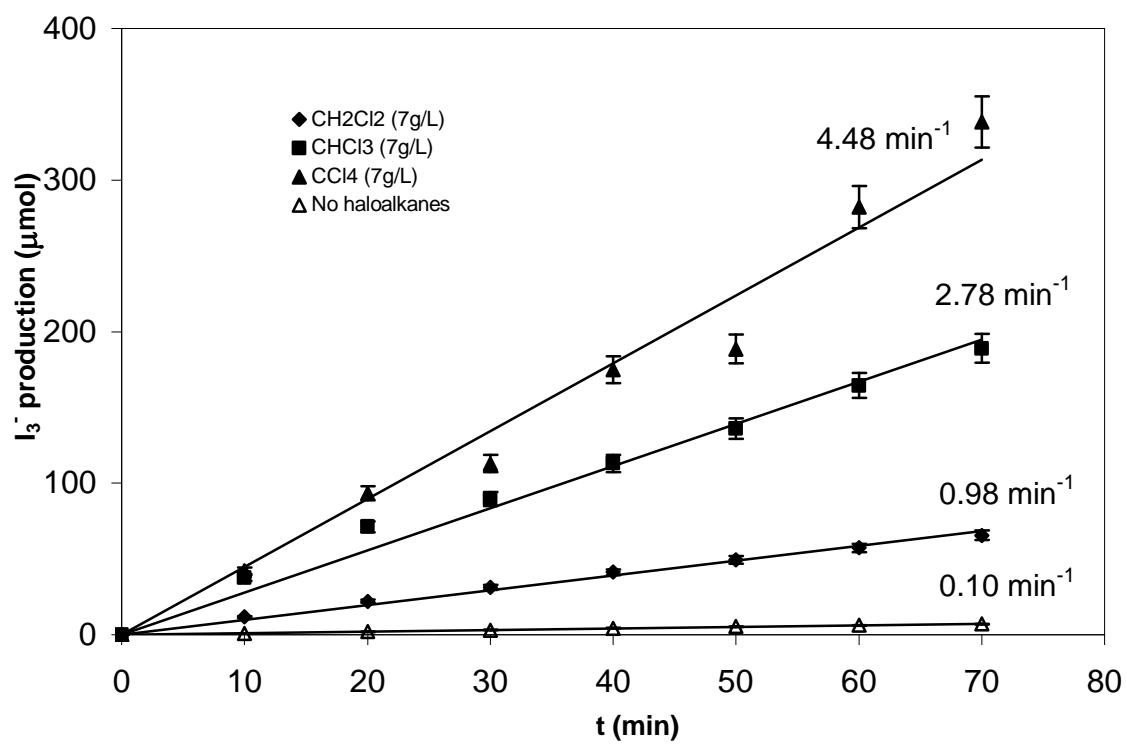


Fig. 5: